

What is claimed is:

## 1. A method of curing

a composition comprising

- (a) at least one free-radical-polymerisable compound or
- (b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or
- (c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c); and

- (d) at least one photolabile compound that is activatable by plasma discharge;

wherein

the composition is applied to a three-dimensional substrate and

the curing is carried out in a plasma discharge chamber.

## 2. A method of curing

a composition comprising

- (a) at least one free-radical-polymerisable compound or
- (b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or
- (c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c);

- (d) at least one photolabile compound that is activatable by plasma discharge; and

- (e) at least one light stabiliser compound or UV absorber compound;

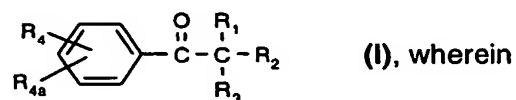
wherein

the curing is carried out in a plasma discharge chamber.

3. A method according to either claim 1 or claim 2, wherein component (d) in the composition is a free-radical photoinitiator, a photolabile acid or a photolabile base.

4. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound selected from the group of benzophenones, benzophenone derivatives, acetophenone, acetophenone derivatives, halomethylbenzophenones, halomethylarylsulfones, dialkoxyacetophenones, anthracene, anthracene derivatives, thioxanthone, thioxanthone derivatives, 3-ketocoumarin, 3-ketocoumarin derivatives, anthraquinone, anthraquinone derivatives,  $\alpha$ -hydroxy- or  $\alpha$ -amino-acetophenone derivatives,  $\alpha$ -sulfonylacetophenone derivatives, 4-aroxy-1,3-dioxolanes, benzoin alkyl ethers and benzilketals, phenyl glyoxalates and derivatives thereof, dimeric phenyl glyoxalates, peresters, monoacylphosphine oxides, bisacylphosphine oxides, trisacylphosphine oxides, halomethyltriazines, titanocenes, borate compounds, O-acyloxime compounds, camphorquinone derivatives, iodonium salts, sulfonium salts, iron aryl complexes, oximesulfonic acid esters and photolabile amines.

5. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula I, II, III or/and IV



**R<sub>1</sub>** is C<sub>1</sub>-C<sub>12</sub>alkyl or C<sub>1</sub>-C<sub>12</sub>alkoxy;

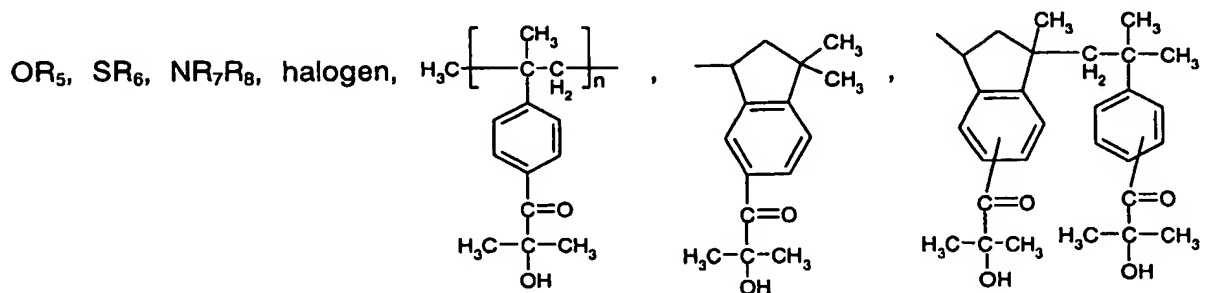
**R<sub>2</sub>** is phenyl, OR<sub>5</sub> or NR<sub>7</sub>R<sub>8</sub>;

**R<sub>3</sub>** has one of the definitions given for R<sub>1</sub> or is C<sub>3</sub>-C<sub>12</sub>alkenyl, phenyl-C<sub>1</sub>-C<sub>6</sub>alkyl or C<sub>1</sub>-C<sub>6</sub>alkylphenyl-C<sub>1</sub>-C<sub>6</sub>alkyl;

or R<sub>1</sub> and R<sub>3</sub>, together with the carbon atom to which they are bonded, form a cyclohexyl ring;

R<sub>2</sub> being phenyl when R<sub>1</sub> and R<sub>3</sub> are both alkoxy;

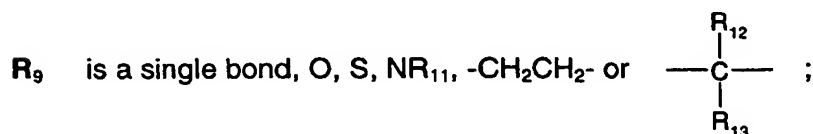
$R_4$  and  $R_{4a}$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ hydroxyalkyl,



$n$  is a number from 1 to 10;

$R_5$  and  $R_6$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkenyl, phenyl, benzyl,  $Si(CH_3)_3$  or  $-[C_aH_{2a}X]_b-R_{10}$ ;

$R_7$  and  $R_8$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl or  $C_2$ - $C_5$ hydroxyalkyl, or  $R_7$  and  $R_8$ , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or a  $NR_{11}$  group;



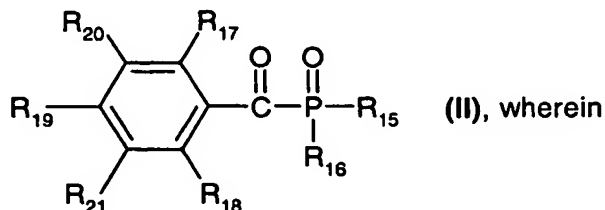
$a$  and  $b$  are each independently of the other a number from 1 to 12;

$X$  is S, O or  $NR_{11}$ ;



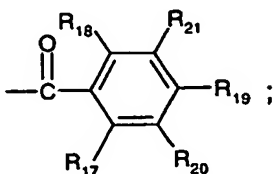
$R_{11}$  is hydrogen, phenyl, phenyl- $C_1$ - $C_4$ alkyl,  $C_1$ - $C_{12}$ alkyl or  $C_2$ - $C_5$ hydroxyalkyl; and

$R_{12}$ ,  $R_{13}$  and  $R_{14}$  are each independently of the others hydrogen or methyl;



$R_{15}$  and  $R_{16}$  are each independently of the other  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkoxy; phenyl which is unsubstituted or substituted by one or more  $OR_{22}$ ,  $SR_{23}$ ,  $NR_{24}R_{25}$ ,  $C_1$ - $C_{12}$ alkyl or halogen

substituents; or  $R_{15}$  and  $R_{16}$  are biphenyl, naphthyl, phenyl- $C_1$ - $C_4$ alkyl or

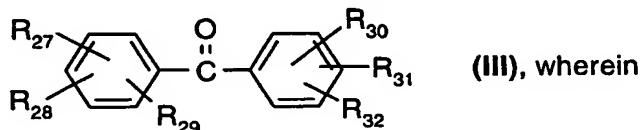


$R_{17}$  and  $R_{18}$  are each independently of the other  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkoxy,  $CF_3$  or halogen;

$R_{19}$ ,  $R_{20}$  and  $R_{21}$  are each independently of the others hydrogen,  $C_1$ - $C_{12}$ alkyl,  $C_1$ - $C_{12}$ alkoxy,  $CF_3$  or halogen;

$R_{22}$ ,  $R_{23}$ ,  $R_{24}$  and  $R_{25}$  are each independently of the others hydrogen,  $C_1$ - $C_{12}$ alkyl,  $C_2$ - $C_{12}$ -alkenyl,  $C_3$ - $C_8$ cycloalkyl, phenyl, benzyl, or  $C_2$ - $C_{20}$ alkyl which is interrupted by O atoms and is unsubstituted or substituted by OH or/and SH; or  $R_{24}$  and  $R_{25}$ , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O or S atoms or an  $NR_{26}$  group; and

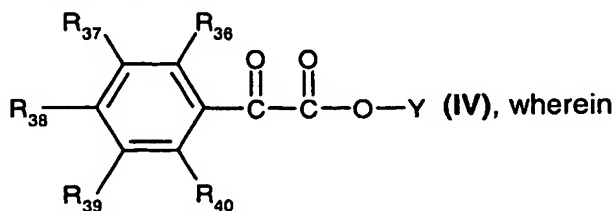
$R_{26}$  is hydrogen, phenyl, phenyl- $C_1$ - $C_4$ alkyl,  $C_1$ - $C_{12}$ alkoxy,  $C_1$ - $C_{12}$ alkyl or  $C_1$ - $C_{12}$ hydroxyalkyl;



$R_{27}$ ,  $R_{28}$ ,  $R_{29}$ ,  $R_{30}$ ,  $R_{31}$  and  $R_{32}$  are each independently of the others hydrogen,  $C_1$ - $C_4$ alkyl, phenyl, naphthyl,  $-OR_{35}$ ,  $-SR_{35}$ ,  $-(CO)O(C_1$ - $C_4$ alkyl), halogen,  $NR_{33}R_{34}$  or a monovalent linear or branched siloxane radical, or  $R_{29}$  and  $R_{30}$ , each in the o-position to the carbonyl group, together form a S atom; and

$R_{33}$  and  $R_{34}$  are each independently of the other hydrogen,  $C_1$ - $C_4$ alkyl,  $C_2$ - $C_6$ hydroxyalkyl, or  $R_{33}$  and  $R_{34}$ , together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or a  $NR_{11}$  group; and

$R_{35}$  is  $C_1$ - $C_{12}$ alkyl,  $C_2$ - $C_6$ hydroxyalkyl or phenyl;



$R_{36}$ ,  $R_{37}$ ,  $R_{38}$ ,  $R_{39}$  and  $R_{40}$  are each independently of the others hydrogen,  $C_1$ - $C_{12}$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, phenyl, naphthyl, halogen, CN and/or by  $-OCOR_{41}$ , or  $C_2$ - $C_{12}$ alkyl which is interrupted by one or more O atoms, or  $R_{36}$ ,  $R_{37}$ ,  $R_{38}$ ,  $R_{39}$

and  $R_{40}$  are  $OR_{42}$ ,  $SR_{43}$ ,  $NR_{44}R_{45}$ , halogen, a monovalent linear or branched siloxane radical, or phenyl unsubstituted or substituted by one or two  $C_1$ - $C_4$ alkyl or/and one or two  $C_1$ - $C_4$ -alkoxy substituents, it being possible for the substituents  $OR_{42}$ ,  $SR_{43}$ ,  $NR_{44}R_{45}$  to form 5- or 6-membered rings by way of the radicals  $R_{42}$ ,  $R_{43}$ ,  $R_{44}$  and/or  $R_{45}$  with further substituents on the phenyl ring or with one of the carbon atoms of the phenyl ring;

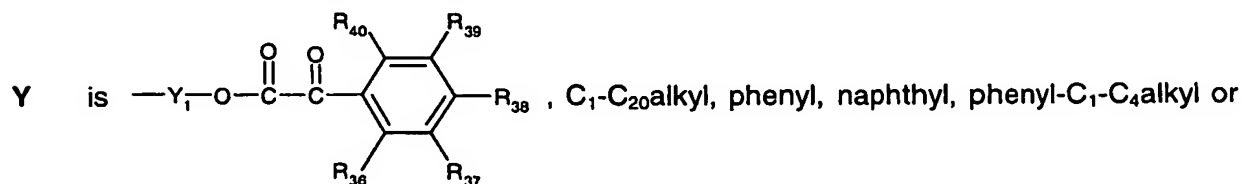
$R_{41}$  is  $C_1$ - $C_8$ alkyl, or phenyl unsubstituted or substituted by from one to three  $C_1$ - $C_4$ alkyl and/or one to three  $C_1$ - $C_4$ alkoxy substituents;

$R_{42}$  and  $R_{43}$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, phenyl, phenoxy or/and by  $-OCOR_{41}$ , or  $C_2$ - $C_{12}$ alkyl which is interrupted by one or more O atoms, or  $R_{42}$  and  $R_{43}$  are phenyl unsubstituted or substituted by  $C_1$ - $C_4$ alkoxy, phenyl or/and by  $C_1$ - $C_4$ alkyl, or  $R_{42}$  and  $R_{43}$  are  $C_3$ - $C_6$ alkenyl, cyclopentyl, cyclohexyl or naphthyl;

$R_{44}$  and  $R_{45}$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy or/and by phenyl, or  $C_2$ - $C_{12}$ alkyl which is interrupted by one or more O atoms, or  $R_{44}$  and  $R_{45}$  are phenyl,  $-COR_{41}$  or  $SO_2R_{46}$ , or  $R_{44}$  and  $R_{45}$ , together with the nitrogen atom to which they are bonded, form a 5-, 6- or 7-membered ring, which may also be interrupted by  $-O-$  or  $-NR_{47}-$ ;

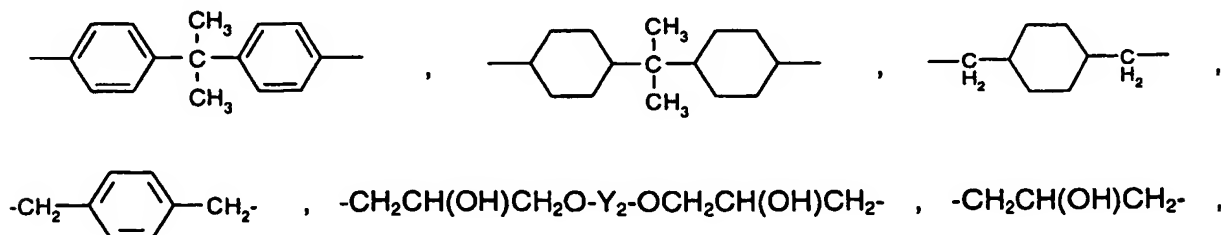
$R_{46}$  is  $C_1$ - $C_{12}$ alkyl, phenyl or 4-methylphenyl;

$R_{47}$  is hydrogen,  $C_1$ - $C_8$ alkyl unsubstituted or substituted by OH or by  $C_1$ - $C_4$ alkoxy, or is phenyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkyl or by  $C_1$ - $C_4$ alkoxy;

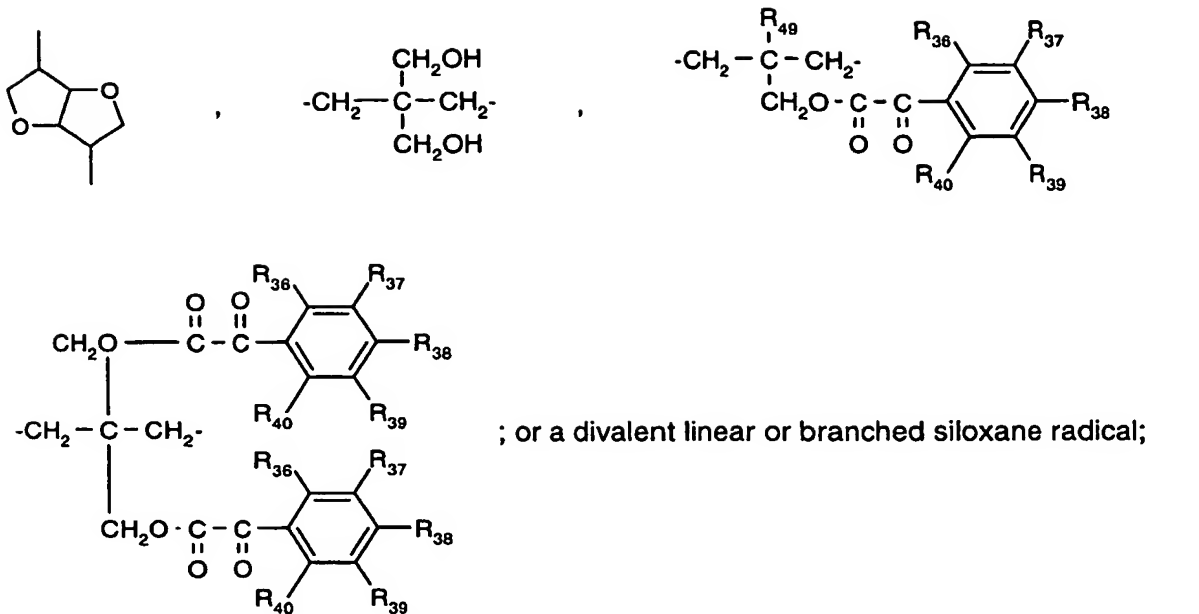


a monovalent linear or branched siloxane radical;

$Y_1$  is  $C_1$ - $C_{12}$ alkylene,  $C_4$ - $C_8$ alkenylene,  $C_4$ - $C_8$ alkynylene, cyclohexylene,  $C_4$ - $C_{40}$ alkylene interrupted by one or more  $-O-$ ,  $-S-$  or  $-NR_{48}-$ , or is phenylene or  $Y_1$  is a group



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**Y<sub>2</sub>** has the same definitions as **Y<sub>1</sub>** with the exception of the formula

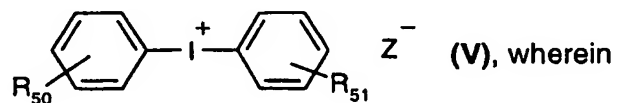
$-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-\text{Y}_2-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$  ;

**R<sub>48</sub>** is hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl or phenyl; and

**R<sub>49</sub>** is hydrogen, CH<sub>2</sub>OH or C<sub>1</sub>-C<sub>4</sub>alkyl.

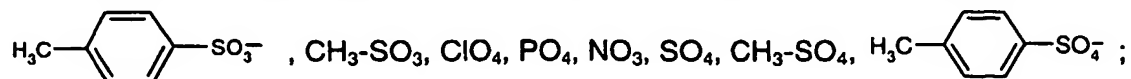
6. A method according to claim 4, wherein component (d) in the composition is at least one compound of formula I or/and II, especially a mixture of a compound of formula I and a compound of formula II.

7. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula V, VI, VII or/and VIIa

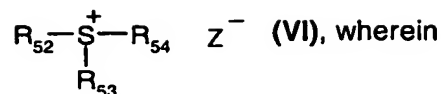


**R<sub>50</sub>** and **R<sub>51</sub>** are each independently of the other hydrogen, C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>1</sub>-C<sub>20</sub>alkoxy, OH-substituted C<sub>1</sub>-C<sub>20</sub>alkoxy, halogen, C<sub>2</sub>-C<sub>12</sub>alkenyl, cycloalkyl, especially methyl, isopropyl or isobutyl; and

**Z** is an anion, especially PF<sub>6</sub>, SbF<sub>6</sub>, AsF<sub>6</sub>, BF<sub>4</sub>, (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B, Cl, Br, HSO<sub>4</sub>, CF<sub>3</sub>-SO<sub>3</sub>, F-SO<sub>3</sub>,

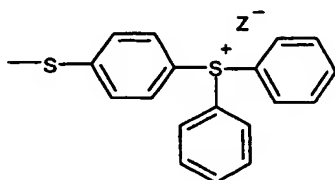


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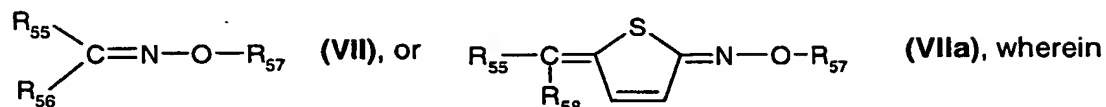


$\text{R}_{52}$ ,  $\text{R}_{53}$  and  $\text{R}_{54}$  are each independently of the others unsubstituted phenyl, or phenyl sub-

stituted by -S-phenyl or by



$\text{Z}^-$  is as defined above;



$\text{R}_{55}$  is  $\left[ \text{C}(\text{O}) \right]_q \text{R}_{58}$ , (CO)O-C<sub>1</sub>-C<sub>4</sub>alkyl, CN or C<sub>1</sub>-C<sub>12</sub>haloalkyl;

$\text{R}_{58}$  has one of the definitions given for  $\text{R}_{55}$  or is  $\text{---} \text{C}_6\text{H}_4 \text{---} \text{O} \text{---} (\text{CH}_2)_3 \text{---} \text{O} \text{---} \text{C}_6\text{H}_4 \text{---} \underset{\text{R}_{55}}{\text{C}}=\text{N}-\text{O}-\text{R}_{57}$ ;

$\text{R}_{57}$  is C<sub>1</sub>-C<sub>18</sub>alkylsulfonyl, C<sub>1</sub>-C<sub>10</sub>haloalkylsulfonyl, camphorylsulfonyl, phenyl-C<sub>1</sub>-C<sub>3</sub>alkylsulfonyl, C<sub>3</sub>-C<sub>30</sub>cycloalkylsulfonyl, phenylsulfonyl, naphthylsulfonyl, anthracylsulfonyl or phenanthrylsulfonyl, the groups cycloalkyl, phenyl, naphthyl, anthracyl and phenanthryl of the radicals C<sub>3</sub>-C<sub>30</sub>cycloalkylsulfonyl, phenyl-C<sub>1</sub>-C<sub>3</sub>alkylsulfonyl, phenylsulfonyl, naphthylsulfonyl, anthracylsulfonyl and phenanthrylsulfonyl being unsubstituted or substituted by one or more halogen, C<sub>1</sub>-C<sub>4</sub>haloalkyl, CN, NO<sub>2</sub>, C<sub>1</sub>-C<sub>16</sub>alkyl, phenyl, C<sub>1</sub>-C<sub>4</sub>alkylthio, C<sub>1</sub>-C<sub>4</sub>alkoxy, phenoxy, C<sub>1</sub>-C<sub>4</sub>alkyl-O(CO)-, C<sub>1</sub>-C<sub>4</sub>alkyl-(CO)O-, R<sub>67</sub>OSO<sub>2</sub>- and/or -NR<sub>60</sub>R<sub>61</sub> substituents; or

$\text{R}_{57}$  is C<sub>2</sub>-C<sub>6</sub>haloalkanoyl, halobenzoyl,  $\text{---} \overset{\text{X}_1}{\underset{\text{R}_{63}}{\text{P}}} \text{---} \text{R}_{64}$ ,  $\text{---} \overset{\text{X}_1}{\underset{\text{X}_2-\text{R}_{65}}{\text{P}}} \text{---} \text{R}_{64}$  or  $\text{---} \overset{\text{X}_1}{\underset{\text{X}_2-\text{R}_{65}}{\text{P}}} \text{---} \text{X}_3-\text{R}_{66}$ ;

$\text{X}_1$ ,  $\text{X}_2$  and  $\text{X}_3$  are each independently of the others O or S;

$q$  is 0 or 2; and

**R<sub>58</sub>** is C<sub>1</sub>-C<sub>12</sub>alkyl, cyclohexyl, camphoryl, unsubstituted phenyl, or phenyl substituted by one or more halogen, C<sub>1</sub>-C<sub>12</sub>alkyl, OR<sub>59</sub>, SR<sub>59</sub> or NR<sub>60</sub>R<sub>61</sub> substituents;

**R<sub>59</sub>** is C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>12</sub>hydroxyalkyl;

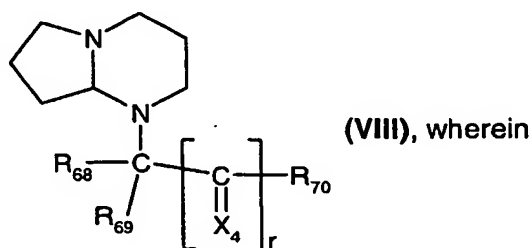
**R<sub>60</sub>** and **R<sub>61</sub>** are each independently of the other hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>2</sub>-C<sub>6</sub>hydroxyalkyl, or **R<sub>60</sub>** and **R<sub>61</sub>**, together with the N atom to which they are bonded, form a 5- or 6-membered ring, which may also contain O atoms or an NR<sub>62</sub> group;

**R<sub>62</sub>** is hydrogen, phenyl, phenyl-C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>alkyl or C<sub>2</sub>-C<sub>5</sub>hydroxyalkyl;

**R<sub>63</sub>**, **R<sub>64</sub>**, **R<sub>65</sub>** and **R<sub>66</sub>** are each independently of the others C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl; or phenyl unsubstituted or substituted by C<sub>1</sub>-C<sub>4</sub>alkyl or by halogen; and

**R<sub>67</sub>** is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, phenyl or tolyl.

8. A method according to either claim 1 or claim 2, wherein component (d) in the composition is at least one compound of formula VIII



**r** is 0 or 1;

**X<sub>4</sub>** is CH<sub>2</sub> or O;

**R<sub>68</sub>** and **R<sub>69</sub>** are each independently of the other hydrogen or C<sub>1</sub>-C<sub>20</sub>alkyl; and

**R<sub>70</sub>** is unsubstituted or C<sub>1</sub>-C<sub>12</sub>alkyl- or C<sub>1</sub>-C<sub>12</sub>alkoxy-substituted phenyl, naphthyl or biphenyl.

9. A method according to either claim 1 or claim 2, wherein the composition comprises, in addition to the photolabile component (d), other additives (h), sensitizer compounds (f) or/and dyes or pigments (g).

10. A method according to claim 1, wherein the composition comprises at least one light stabilizer or/and at least one UV absorber compound.

11. A method according to either claim 1 or claim 2, wherein the composition is a surface coating.



12. A method according to either claim 1 or claim 2, wherein the composition is a printing ink.

13. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component solely free-radical-polymerisable compounds (a).

14. A method according to claim 13, wherein the free-radical-polymerisable compound comprises at least one mono-, di-, tri- or tetra-functional acrylate monomer and/or at least one mono-, di-, tri- or tetra-functional acrylate-functional oligomer.

15. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component solely cationically polymerisable or crosslinkable compounds (b).

16. A method according to either claim 1 or claim 2, wherein the composition comprises as polymerisable component a mixture of at least one free-radical-polymerisable compound (a) and at least one cationically polymerisable compound (b).

17. A coated substrate which is coated on at least one surface by means of the method according to either claim 1 or claim 2.

18. A coating obtainable by a method according to either claim 1 or claim 2.

19. A method of curing

a composition comprising

(1) a combination of at least one electron acceptor compound, especially a maleimide compound, and at least one electron donor compound, especially a vinyl ether compound; and

(2) optionally at least one free-radical-polymerisable compound (a),

wherein the curing is carried out in a plasma discharge chamber.

20. A method of curing

a composition comprising

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(a) at least one free-radical-polymerisable component having at least one ethylenically unsaturated double bond, the free-radical-polymerisable component optionally additionally being functionalised with OH, NH<sub>2</sub>, COOH, epoxy or NCO groups; and

(a1) at least one polyacrylate or/and polyester polyol in combination with melamine or with a melamine derivative, or in combination with a blocked or non-blocked polyisocyanate; or

(a2) at least one carboxyl-, anhydride- or amino-functional polyester or/and at least one carboxyl-, anhydride- or amino-functional polyacrylate in combination with an epoxy-functional polyester or polyacrylate; or

(a3) a mixture of (a1) and (a2);

(d) at least one photolabile compound that is activatable by plasma discharge;

wherein

the curing of the composition is carried out in a plasma discharge chamber and, optionally, thermal pre- or after-treatment is carried out.

21. A method of producing mouldings from composite materials, wherein a support is impregnated with a composition comprising

(a) at least one free-radical-polymerisable compound or

(b) at least one compound that, under the action of an acid, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

(c) at least one compound that, under the action of a base, is able to enter into a polymerisation, polycondensation or polyaddition reaction, or

a mixture of components (a) and (b), or

a mixture of components (a) and (c); and

(d) at least one photolabile compound that is activatable by plasma discharge;

and is introduced into a mould;

wherein the curing is carried out in a plasma discharge chamber and, optionally, thermal aftertreatment is carried out.